



## ***Interactive comment on “Versatile soil gas concentration and isotope monitoring: optimization and integration of novel soil gas probes with online trace gas detection” by Juliana Gil-Loaiza et al.***

**Juliana Gil-Loaiza et al.**

juligil@email.arizona.edu

Received and published: 1 April 2021

Dear Dr. Nicolas Brüggemann and Reviewer #2,

We appreciate the positive comments and the reviewer's #2 consideration of that innovation in soil probes and soil trace gases instrumentation is very important. Following, we will address each of the reviewers comments and suggestions, those that required edits to the manuscripts will be addressed and will be noted in each response if pertinent for the editors' evaluation.

C1

RC2: Is there still control air coming through the bottom of the column when the probe is incubated in soil, or only for flushing the column for rapid redox state shifts?

Answer: The reviewer brings up a good point for us to clarify in the text and Table 4. In tests with silica (Table 3), we continually fluxed the matrix with control gas to provide our 'gold standard' for comparison to soil probe measurements. In soil experiments (Table 4) the control air was added to quickly change redox conditions and stopped prior to measurements. We have clarified these experimental details by adjusting columns in Table 4 to more clearly list the control gas and its purpose.

RC2: Can the authors add in a sentence about the response/equilibrium time (if it can be deduced from the flow rates) for the gasses in the system in the setups shown, and how does that compare to other published probe setups? This would be especially important for highly temporally dynamic and depth stratified systems.

Answer: In the open flow-through probe sampling approach described here, soil probes have time to equilibrate with soil before being sampled, so that when selected, the most fully equilibrated sample is initially observed (e.g., Fig. 5 at time 00:31). As the flow-through sampling progresses, gas concentrations sampled via the probe come to steady state values proportional to soil gas concentration and inversely proportional to flow rate (Fig. 6). In steady state, sampling duration does not increase equilibration and there is no equilibration time we can report.

In contrast, closed-path recirculating flow-through sampling can progressively come closer to equilibration with every pass. For example, DeSutter, Sauer, and Parkin 2006 (doi:10.1016/j.soilbio.2006.04.022) provide a nice evaluation of extruded PTFE vs Polyethylene (PE) tubing in a closed pass setup with a CO<sub>2</sub> sensor and report the time of 95% equilibrium ( $t_{eq}$ ) of CO<sub>2</sub>.

Here, we can calculate the residence time of carrier gas in the soil probe by considering the internal volume of the probes ( $V=2.6\text{--}4.6$  mL) and the range of flow rates evaluated ( $F=5\text{--}300$  sccm). This indicates that the residence time ( $V/F$ ) could range

C2

from <1 sec for high flow rates to 55 sec for the lowest flow rates and larger volume (5 sccm in probes P5, P8, P10). We agree with the reviewer that this is helpful information to provide because it helps explain the dependence on probe flow rate (Fig. 6), and we can add the residence times of gas in the probe (lines TBD). We note that even the lowest residence times are actually very fast, and would be suitable for highly temporally dynamic and depth-stratified systems.

RC2: Why did the authors choose to sample destructively in the soil setup rather than recirculating the air through the column after going through the TILDAS? It doesn't seem like TILDAS is a destructive method so a closed system should be possible (and possibly more desirable) for the soil experiment and more amenable to translating the setup to controlled in-situ studies. I would assume that an open system with fresh ultra zero air would just generate a concentration gradient and accelerate influx, such that the relative difference between actual and perceived gas concentration would be greater at high flow rates compared to low flow rates after accounting for dilution. But that there is also a counteracting equilibration time effect at fast flow rates (which is what is shown in figure 4 and 6, without necessarily parsing out the magnitude of concentration gradient and time to equilibrium effects).

Answer: For this initial study we wanted to evaluate the integration of the sintered PTFE soil probes and the new TILDAS with a reduced sample cell volume with a continuous method, which can be less complex for field deployment and less prone to create artifacts during sampling. Additionally, using the open flow-through method will allow the analysis of the same sample by other instruments connected in-line with TILDAS like PTR-MS Vocus-GC instruments. We kindly refer the reviewer to the previous response to clarify the equilibration time effect at fast flow rates.

RC2: Maybe something to speculate on whether it would be possible to make the detector volumes even smaller so that the probe volumes could be smaller and perhaps depth-resolved, or whether the whole system would need to be re-developed. This would be a really useful for any system where the soil is strongly depth resolved in

C3

terms of chemistry and/or temperature (ex thawing tundra or forest floor).

Answer: We appreciate the reviewer's suggestion. We agree that decreasing the analyzer volume demand has been a challenge for soil trace gas detection in soils and the previous sampling systems using diffusive sample transfer. Laser spectrometers still require sufficient pathlength to quantify trace amounts of N<sub>2</sub>O isotopes, for example, so there is a trade-off between cell volume size and pathlength that we addressed here with the novel volume reducing insert. There is promise to reduce sample cells and pathlengths for some trace gases, especially when not determining isotopes. We are currently challenging the sampling system spatial resolution in both laboratory and field studies, which will be the topic of future papers.

RC2: Soil texture for S1: if the clay+silt = 66%, then the sand cannot be > 34%. L600 with rather than without?

Answer: We agree, the reviewer makes a good point. To avoid confusion, we will add the following phrase "predominant soil texture is sandy clay loam (20-35% clay-loam and remaining fraction sand" In table S1

---

Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2020-401>, 2020.

C4